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**PATENT SPECIFICATION** **616,523**



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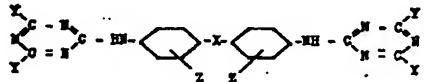
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**COMPLETE SPECIFICATION**

**Manufacture of Direct Dyestuffs and Intermediates**

We, J. R. GEIGY A. G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the 5 nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

According to this invention valuable 10 new dyestuffs or intermediates of the stilbene or dibenzyl series are made by treating a condensation product of the general formula



15 in which X represents  $-\text{CH}=\text{CH}-$  or  $-\text{CH}_2-\text{CH}_2-$ , Y represents a halogen atom, and both of the Z's represent H or  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$ , with at least one aromatic 20 amine so as to exchange at least one halogen atom for the residue of an amino-azo-compound or for the residue of an amine which, after the exchange, is capable of forming azo-dyestuffs, and by 25 treatment with ammonia and/or amines exchanging any other halogen atoms for amino groups or the residues of amines or in part for amino groups and in part for the residues of amines, which amine residues may contain azo-groups and, in 30 the case of a plurality of amine residues, may be identical or different from one another.

Among the residues of amines which 35 are capable, after the exchange referred to above, of forming azo-dyestuffs there are to be understood those which contain a further diazotizable amino-group or a group which is convertible by saponification or reduction into such an amino-group, or which contain substituents

which enable coupling with suitable diazo-components to be brought about. This coupling may be performed in substance or on the fibre. It will be understood that the amines or amino-azo-compounds whose residues are to be introduced into the condensation product of the aforesaid general formula may also contain one or more groupings which 50 enable metallisation to be brought about on the fibre or in substance. Alternatively, a metallisable group may be subsequently introduced into the molecule by diazotising an amine containing 55 a metallisable group in ortho-position, for example, an ortho-amino-carboxylic acid or an ortho-aminophenol, and coupling the diazo-compound with a condensation product containing a component 60 capable of coupling in ortho-position to a hydroxyl group, for example, the residue of an amino-naphthol sulphonic acid.

The new dyestuffs dye cellulose direct, and are distinguished, in general, by good 65 capacity for absorption and, even in direct dyeing, by good fastness to water and washing. Moreover, it is surprising that in most cases the fastness to water and washing is in part considerably 70 improved by after-treatment with a little formaldehyde.

By the process of the invention, which affords numerous possibilities for variation, dyestuffs can be obtained which, 75 depending on the nature of the components used, dye cellulose fibres chiefly yellow, orange, red, violet or brown tints, and which are suitable for diazotising and coupling, for coupling with 80 diazotised amines, for treatment with metal salts on the fibre or in substance, or, as already stated, for after-treatment with formaldehyde. More especially, therefore, various types of dyestuffs 85 capable of after-treatment can be made, of which the after-treated dyeings are distinguished by good to very good wet-

fastness properties. Especially suitable metal salts for after-treatment of the dyestuffs on the fibre are salts of trivalent or hexavalent chromium, and also copper salts. The dyestuffs in the yellow range, more especially, yield dyeings which when after-treated with chromium salts are distinguished in part by their very pure shade. Finally, it may also be mentioned that more especially the dyestuffs suitable for after-treatment with formaldehyde or chromium salts possess the valuable property of almost completely reserving animal fibres, so that these dyestuffs are of particular value for use in conjunction with suitable wool dyestuffs, especially with wool dyestuffs capable of being chromed, for dyeing mixtures or mixed fabrics of cellulose fibres and animal fibres.

The invention is illustrated in the following Examples and Tables, the parts being by weight:

EXAMPLE 1.

25 37 parts of cyanuric chloride are caused to react, in the form of a fine aqueous suspension with a neutral solution of 37 parts of 4:4<sup>1</sup> - diaminostilbene - 2:2<sup>1</sup>-disulphonic acid at 0-4° C. under 30 neutral conditions. The di-primary condensation product is further condensed with a neutral solution of 55.4 parts of 4 - amino - 1:1<sup>1</sup>-azobenzene-3<sup>1</sup>-sulphonic acid at 40-42° C., the reaction being 35 maintained neutral by the addition of sodium carbonate. A di-tertiary condensation product is then formed by reaction with an excess of dimethylamine at a temperature of 85-95° C., and is 40 isolated by precipitation with common salt.

The dried dyestuff is a yellow powder which dissolves with a yellow coloration in water, and dyes cellulose fibres yellow tints of good fastness to light. By treatment with formaldehyde on the fibre the wet-fastness properties are considerably improved.

EXAMPLE 2.

50 37 parts of cyanuric chloride are caused to react with 37 parts of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid to form the di-primary condensation product. The next pair of halogen atoms are 55 replaced by reaction in the usual way with 92.8 parts of the monoazo-dyestuff from diazotised 2-aminonaphthalene-4:8-disulphonic acid and 1-amino-3-acetylaminobenzene. A di-tertiary condensation product is formed by reaction with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate on a boiling waterbath.

The dried dyestuff is an orange powder

which dissolves with an orange coloration 65 in water, and dyes cellulose fibres reddish yellow tints of good wet fastness and good fastness to light. The wet fastness can be further improved by after-treatment with formaldehyde.

EXAMPLE 3.

The condensation product from 37 parts of cyanuric chloride and 37 parts of 4:4<sup>1</sup> - diaminostilbene - 2:2<sup>1</sup>-disulphonic acid is caused to react with 54.2 parts of 75 4 - amino - 3 - methoxy-1:1<sup>1</sup>-azobenzene-3<sup>1</sup>-carboxylic acid in known manner. A di-tertiary condensation product is made by further condensation with 30 parts of 3 - acetylaminol - 1 - aminobenzene in the 80 presence of 30 parts of crystalline sodium acetate at 85-95° C.

The dyestuff is a brown powder which dissolves with a yellow coloration in water, and dyes cellulose fibres yellow 85 tints of good wet fastness properties, which can be further improved by after-treatment with formaldehyde.

By saponifying the acetyl groups of the dyestuff, for example, by boiling with 90 caustic soda solution of 5 per cent. strength for one hour, a product is obtained of which the dyeings can be diazotised and developed. Thus, for example, yellow tints of good fastness to 95 water and washing are obtained by development with 1 - phenyl - 3 - methyl - 5-pyrazolone.

EXAMPLE 4.

The condensation product obtained 100 from 37 parts of cyanuric chloride and 37 parts of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid is further condensed with 124.2 parts of the monoazo-dyestuff from 1 - diazo-8-(para-toluene-sulpho)-105 oxynaphthalene-3:6-disulphonic acid and 1 - amino - 3 - methyl-6-methoxy-benzene. The last two chlorine atoms are caused to react with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate. The di-tertiary condensation product is salted out, the para-toluene-sulpho-group is split off in alkaline solution, and the dyestuff is isolated.

The dried dyestuff is a dark red powder 115 which dissolves with a red coloration in water, and dyes cellulose fibres red tints. Dyeings of good fastness to water and washing are obtained by after-treatment with formaldehyde.

EXAMPLE 5.

10.6 parts of sodium carbonate are slowly added at 0°-4° C. to a very fine aqueous suspension of 21 parts of 4:4<sup>1</sup>-diaminostilbene and 37 parts of cyanuric 125 chloride. When the reaction is complete the whole is further condensed with 124.1 parts of the monoazo-dyestuff from 1-diazo - 8 - (para - toluene - sulpho) - oxy-

5 naphthalene-3:6-disulphonic acid and 1-amino-3-methyl-6-methoxybenzene. A di-tertiary condensation product is made by reaction with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate.

10 The dried dyestuff is a red powder which dissolves with a red coloration in water, and dyes cellulose fibres red tints of good fastness to water, washing and light. The wet fastness properties are improved by after-treatment with formaldehyde.

EXAMPLE 6.

15 The di-secondary condensation product obtained as described in Example 4 from 2 mols. of cyanuric chloride, 1 mol. of 4:4'-diaminostilbene-2:2'-disulphonic acid and 2 mols. of the monoazo-dyestuff 20 from 1-diazo-8-(para-toluene-sulpho)-oxy-naphthalene and 1-amino-3-methyl-6-methoxy-benzene, is condensed in the third stage with 2 mols. of 3-amino-acetanilide, and after saponification a dyestuff with similar properties is obtained. However, this dyestuff can be diazotised and developed on the fibre. Thus, for example, by development with  $\beta$ -naphthol a strong yellowish red dyeing of good 30 fastness to water and washing is obtained.

EXAMPLE 7.

35 The di-primary condensation product from 37 parts of cyanuric chloride and 29.8 parts of 4:4'-diaminostilbene-3:3'-dicarboxylic acid is caused to react in known manner with 73.9 parts of 4-amino-2-acetyl-amino-4'-chloro-1:1'-azobenzene-3'-sulphonic acid to form the 40 di-secondary condensation product, and the latter is then further condensed with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate.

45 The dry dyestuff is a yellow-red powder which dissolves with a yellow-orange coloration in water, and dyes cellulose fibres reddish yellow tints of good fastness to light, washing and water. The wet fastness properties can be further improved by after-treatment with formaldehyde.

EXAMPLE 8.

55 37 parts of cyanuric chloride are condensed in the usual manner with 37 parts of 4:4'-diaminostilbene-2:2'-disulphonic acid, a di-secondary condensation product is formed by reaction with 73.9 parts of 4-amino-2-acetyl-amino-4'-chloro-1:1'-azobenzene-3'-sulphonic acid, and 60 the product is then condensed with 28.5 parts of 1-chloro-2:4-diaminobenzene. A dyestuff is obtained which dissolves with an orange-red coloration in water. It dyes cellulose fibres reddish yellow tints, can 65 be diazotised on the fibre, and on being

developed with 1-phenyl-3-methyl-5-pyrazolone yields reddish-yellow dyeings of good fastness to washing and water.

EXAMPLE 9.

70 37 parts of cyanuric chloride are condensed with 37 parts of 4:4'-diaminostilbene-2:2'-disulphonic acid in known manner. By further reaction with 51.4 parts of 4-amino-4'-oxy-1:1'-azobenzene-3'-carboxylic acid, and condensation of 75 the resulting di-secondary product with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate, a dyestuff is obtained which, when dry, is a yellow brown powder which dissolves 80 with a yellow coloration in water, and dyes cellulose fibres greenish yellow tints. The fastness to washing and water are considerably improved by after-treatment with formaldehyde or chromium salts. 85 More especially by treatment of the dyeings with chromic salts excellent fastness to water and washing is obtained with only a very slight dulling of the shade.

EXAMPLE 10.

90 The product obtained from 37 parts of cyanuric chloride and 37 parts of 4:4'-diaminostilbene-2:2'-disulphonic acid is caused to react with 73.9 parts of 4-amino-2-acetyl-amino-4'-chloro-1:1'-azobenzene-3'-sulphonic acid to form a di-secondary condensation product, and the latter is then further condensed with 30.4 parts of 1-amino-4-oxybenzene-3-carboxylic acid. A dyestuff is obtained which, 95 when dry, is a brown powder, which dissolves with a yellow-orange coloration in water, and dyes cellulose fibres yellow-orange tints, of which the wet fastness properties are further improved by after-treatment with chromium salts. 100

105 A dyestuff with similar properties is obtained by causing the above described di-secondary condensation product from 2 mols. of cyanuric chloride, 1 mol. of 4:4'-diaminostilbene-2:2'-disulphonic acid and 2 mols. of 4-amino-2-acetyl-amino-4'-chloro-1:1'-azobenzene-3'-sulphonic acid to react with 70.4 parts (2 mols.) of 1-(3'-aminobenzoyl)-amino-4'-oxy-3-carboxybenzene-5-sulphonic acid, which can be prepared by acylating 1-amino-4-oxy-3-carboxybenzene-5-sulphonic acid with 3-nitrobenzoyl chloride in aqueous solution and then 110 reducing the product so obtained, for example, with sodium sulphide. Similar dyestuffs are also obtained by replacing the 1-amino-4-oxybenzene-3-carboxylic acid used in the above Example by 1-(4'-aminobenzoyl)-amino-2-oxy-3-carboxybenzene-5-sulphonic acid or by 1-(4'-aminobenzoyl)-amino-4-oxy-3-

carboxybenzene-5-sulphonic acid which can be prepared by acylating 1-amino-4-oxy-3-carboxy-benzene-5-sulphonic acid, with 4-nitrobenzoyl chloride in 5 aqueous solution and reducing, for example, with sodium sulphide.

EXAMPLE 11.

The dipimary condensation product from 37 parts of cyanuric chloride and 10. 37 parts of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid is caused to react in known manner with 64.6 parts of 4-amino-2-methoxy-2<sup>1</sup>-oxy-1:1<sup>1</sup>-azobenzene-5<sup>1</sup>-sulphonic acid, and the 15 resulting product is condensed with 30.4 parts of 1-amino-4-oxybenzene-3-carboxylic acid to form a di-tertiary product. The dried dyestuff is a brown powder which dissolves with a brown-yellow 20 coloration in water, and dyes cellulose fibres brown-yellow tints. By after-coupling on the fibre red-brown tints of excellent fastness to light are obtained. If the copper complex is prepared in 25 substance, for example, with a slightly acid reaction to Congo, a dark red powder is obtained which dyes cellulose fibres brownish red tints.

EXAMPLE 12.

30. 37 parts of cyanuric chloride are condensed with 37 parts of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid, the product is then condensed with 47.8 parts of 2-amino-5-oxynaphthalene-7-sulphonic acid, and the two chlorine atoms in the secondary condensation product are caused to react with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate. A pale grey 40 substance is obtained. By coupling with diazotised 1-aminobenzene-2-carboxylic acid in a solution rendered alkaline with sodium carbonate, a red-brown dyestuff is obtained, which dissolves with an orange 45 coloration in water, and dyes cellulose fibres orange tints. By treatment on the fibre with copper sulphate red-brown dyeings of good wet fastness properties and very good fastness to light are obtained. 50 The copper complex may also be prepared in substance.

Similar dyestuffs are obtained by using, instead of 2-amino-5-oxy-naphthalene-7-sulphonic acid, 2-amino-8-oxy-naphthalene-6-sulphonic acid or (N)-aminobenzoylated derivatives. Moreover, the two chlorine atoms in the secondary product may be exchanged for para-aminosalicylic acid, dimethylamine, or 60 3-aminoaminoacetanilide.

The condensation products described in the above Example, for example, that from 2 mols. of cyanuric chloride, 1 mol. of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic

acid, 2 mols. of 2-amino-5-oxynaphthalene-7-sulphonic acid and 2 mols. of aniline, can be applied to cellulose fibres by the usual dyeing processes, and developed with diazotised para-nitraniline or other diazo-compounds. Orange to red 70 tints of good fastness properties are obtained.

EXAMPLE 13.

37 parts of cyanuric chloride and 37 parts of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid are caused to react in known manner to form a di-primary condensation product. The latter is further condensed with 89.4 parts of the disazo-dye-stuff prepared in known manner by coupling diazotised 4-amino-1:1<sup>1</sup>-azobenzene with 2-amino-5-oxynaphthalene-7-sulphonic acid in an alkaline medium, and a di-tertiary condensation product is prepared by reaction with 34.6 parts of 85 metanilic acid.

The dried dyestuff is a dark red powder, which dissolves with a red coloration in water, and dyes cellulose fibres bluish red tints of which the fastness to washing is improved by treatment with formaldehyde.

EXAMPLE 14.

The condensation product obtained as described in Example 12 from 2 mols. of 95 cyanuric chloride, 1 mol. of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid, 2 mols. of 2-amino-5-oxynaphthalene-7-sulphonic acid and 2 mols. of aniline is coupled with diazotised 4-amino-1:1<sup>1</sup>-azobenzene in a weakly alkaline solution.

The dried dyestuff is a dark red powder, which dissolves with a red coloration in water, and dyes cellulose fibres bluish red tints. The wet fastness properties can be further improved by after-treatment with formaldehyde.

EXAMPLE 15.

The condensation product from 37 parts of cyanuric chloride and 37 parts of 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acid is caused to react in known manner with 75.6 parts of 4-amino-2-methyl-6-methoxy-4<sup>1</sup>-acetylarnino-1:1<sup>1</sup>-azobenzene-5<sup>1</sup>-sulphonic acid to form a di-secondary condensation product. The remaining chlorine atoms are caused to react with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate, and the acetyl groups are saponified in 120 alkaline solution, for example, as described in Example 3. The dried dyestuff is a yellow-orange powder, which dissolves with an orange coloration in water, and dyes cellulose fibres yellow-orange tints. Deep orange dyeings of good 125 wet fastness properties are obtained by

diazotising and coupling with 1-phenyl-3-methyl-5-pyrazolone.

EXAMPLE 16.

A neutral solution of 37.2 parts of 4:4'-diaminodibenzyl - 2:2'-disulphonic acid is introduced into a finely dispersed suspension of 37 parts of cyanuric chloride in ice-cold water, and a neutral reaction is maintained by the addition of 10.6 parts of sodium carbonate. The di-primary condensation product is further reacted in the usual manner with 51.4 parts of 4-amino-4'-oxy-1:1'-azobenzene-3'-carboxylic acid and the two remaining chlorine atoms are exchanged for the residues of aniline in the manner described in the preceding Example. The dyestuff formed is a yellow powder, which dissolves with a yellow coloration in water, and dyes cellulose fibres yellow tints. The wet fastness properties are further substantially improved by after-treatment with formaldehyde or with chromium salts.

Other similar dyestuffs are obtained by exchanging the two final chlorine atoms for  $-\text{NH}_2$ , by reaction with ammonia, or for  $\text{CH}_2\text{NH}-$  or  $(\text{CH}_2)_2\text{N}-$  groups or for the residue of the 1-amino-4-oxybenzene-3-carboxylic acid, instead of for aniline residues.

EXAMPLE 17.

37 parts of cyanuric chloride are condensed with 37 parts of 4:4'-diaminostilbene-2:2'-disulphonic acid in the usual manner, and the di-primary condensation product is caused to react with 62.1 parts of the monoazo-dyestuff from 1-diazo-8-(para-toluenesulpho)-oxy-naphthalene-3:6-disulphonic acid and 1-amino-3-methyl-6-methoxybenzene. The remaining chlorine atoms are caused to react with 38.7 parts of aniline hydrochloride and 90 parts of crystalline sodium acetate. After splitting off the toluene-sulpho-group the dyestuff is obtained as a dark red powder. It dissolves with a red coloration in water, and dyes cellulose fibres red tints with good wet fastness properties, which can be further improved by treatment with formaldehyde.

A similar product can be obtained, for example, by condensing the diprimary condensation product firstly with 12.9 parts of aniline hydrochloride and 30 parts of crystalline sodium acetate, then with the above described monoazo-dyestuff, and finally with 28.6 parts of monomethylaniline hydrochloride and 60 parts of crystalline sodium acetate.

EXAMPLE 18.

37 parts of cyanuric chloride are caused to react with 37 parts of 4:4'-diamino-

stilbene-2:2'-disulphonic acid. The product is then condensed in the second stage with 25.7 parts of 4-amino-4'-oxy-1:1'-azobenzene-3'-carboxylic acid and 15.2 parts of 1-amino-4-oxybenzene-3-carboxylic acid, and the two remaining chlorine atoms are caused to react with aniline, for example, as described in Example 9. The dried dyestuff is a yellow-brown powder, which dissolves with a yellow coloration in water, and dyes cellulose fibres green-yellow tints of good wet fastness properties, which can be further improved by means of formaldehyde or chromium salts.

EXAMPLE 19.

The di-primary condensation product from 37 parts of cyanuric chloride and 37 parts of 4:4'-diaminostilbene-2:2'-disulphonic acid is caused to react first with 25.7 parts of 4-amino-4'-oxy-1:1'-azobenzene-3'-carboxylic acid, and then with 36.9 parts of 4-amino-2-acetyl-amino-4'-chloro-1:1'-azobenzene-3'-sulphonic acid. The di-secondary condensation product is then condensed with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate. The amino-azo-dyestuffs may be condensed in the reverse order, or the two azo-components may be added simultaneously. The dried dyestuff is a brown powder, which dissolves with a yellow coloration in water, and dyes cellulose fibres yellow tints. The wet fastness properties, which are good, can be further improved by after-treatment with formaldehyde or chromium salts.

EXAMPLE 20.

130 parts of the di-secondary condensation product, described in Example 8, from 2 mols. of cyanuric chloride, 1 mol. of 4:4'-diaminostilbene-2:2'-disulphonic acid and 2 mols. of 4-amino-2-acetyl-amino-4'-chloro-1:1'-azobenzene-3'-sulphonic acid are caused to react with 51.4 parts of 4-amino-4'-oxy-1:1'-azobenzene-3'-carboxylic acid, and the product is freed from any traces of undissolved amino-azo-dyestuffs that may be present by reprecipitation. The dried dyestuff is a brown powder which dissolves with a yellow coloration in water, and dyes cellulose fibres yellow tints. The wet fastness properties can be further improved by treatment with formaldehyde or chromium salts.

EXAMPLE 21.

66.7 parts of the di-primary condensation product from 2 mols. of cyanuric chloride and 1 mol. of 4:4'-diaminostilbene-2:2'-disulphonic acid are condensed in known manner with 100 parts of the

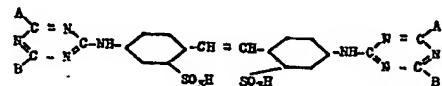
monoazo-dyestuff from diazotised 1-(4<sup>1</sup>-aminobenzoyl)-amino-4-oxy-3-carboxybenzene-5-sulphonic acid, which can be prepared in the manner indicated in Example 10, and 1-amino-3-methyl-6-methoxybenzene. A di-tertiary condensation product is formed by reaction with 25.8 parts of aniline hydrochloride and 60 parts of crystalline sodium acetate.

10 The dry dyestuff is an orange-brown powder, which dissolves with an orange coloration in water, and dyes cellulose fibres reddish yellow tints of good fastness to water and washing. The wet fastness properties can be considerably improved by after-treatment with chromium salts without any marked dulling of the shade taking place.

15 Similar dyestuffs are obtained by using, instead of the monoazo-dyestuff from diazotised 1-(4<sup>1</sup>-aminobenzoyl)-amino-4-oxy-3-carboxybenzene-5-sulphonic acid and 1-amino-3-methyl-6-methoxybenzene,

20 the monoazo-dyestuff from 1-(3<sup>1</sup>-aminobenzoyl)-amino-4-oxy-3-carboxybenzene-5-sulphonic acid, which can be prepared in the manner indicated in Example 10, and 1-amino-3-methyl-6-methoxybenzene or by the monoazo-dyestuff from 1-(4<sup>1</sup>-aminobenzoyl)-amino-4-oxybenzene-3-carboxylic acid and 1-amino-3-methyl-6-methoxybenzene.

In the following Tables are given further dyestuffs obtainable in accordance with the present invention. The dyestuffs in Table I have the general formula



the compounds from which the residues A and B are derived being stated in the Table for each dyestuff.

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TABLE I.

The last column indicates the possible after-treatments which come under consideration.

No.	Compound A	Compound B	Dyeing on cellulose fibres	After-treatments:	
				Me = Metal salts F = Formaldehyde, etc.	
1	4-amino-4 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azobenzene-3 <sup>1</sup> -carboxylic acid	monomethylaniline	greenish yellow	Me. F	
2	„	1 - amino - 4 - oxybenzene - 3 - carboxylic acid	„	Me F	
3	„	3 - amino - acetanilide	„	Me, F, saponified, and developed with 1-phenyl-3-methyl-5-pyrazolone	
4	„	1 - chloro - 2:4-diaminobenzene	greenish yellow	developed with 1-phenyl-3-methyl-5-pyrazolone	
5	4-amino-2-methyl-4 <sup>1</sup> -oxy-3 <sup>1</sup> -carboxy-1:1 <sup>1</sup> -azobenzene-5-sulphonic acid	aniline	yellow	Me F	
6	1-amino-4-oxy-3-carboxybenzene-5-sulphonic acid → 1 - amino-3-methyl-6-methoxybenzene	„	reddish yellow	Me	
7	4-amino-1:1 <sup>1</sup> -azobenzene-3 <sup>1</sup> -sulphonic acid	1-amino - 4 - oxybenzene - 3 - carboxylic acid	yellow	F	

TABLE I. (cont.)

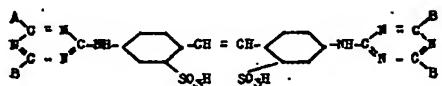
No.	Compound A	Compound B	Dyeing on cellulose fibres	After-treatments:	
				Me = Metal salts F = Formaldehyde, etc.	
8	4-amino-1:1'-azobenzene-3'-sulphonic acid	aniline	yellow		F
9	4-amino - 2 - methyl - 5 - methoxy - 1:1' - azobenzene-4'-sulphonic acid	1-amino - 4 - oxybenzene - 3 - carboxylic acid	„		Me F
10	„	aniline	„		F
11	4-amino-3-methoxy-1:1'-azobenzene-3'-carboxylic acid	„	greenish yellow		F
12	„	1-amino - 4 - oxy-3-carboxy-benzene-5-sulphonic acid	„		Me
13	4 - amino-2-acetylamino-4' - chloro-1:1'-azobenzene-3'-sulphonic acid	aniline	yellow		F
14	„	ammonia	„		F
15	„	dimethylamine	„		F
16	„	3-amino-acetanilide	„		F
17	2 - naphthylamine-4:8- disulphonic acid → 3 - aminoacetanilide	3-amino-acetanilide	reddish yellow		F
18	„	ammonia	„		F
19	„	dimethylamine	„		F
20	„	aniline	„		F
21	„	1-amino - 4 - oxybenzene - 3 - carboxylic acid	„		Me
22	Dyestuff from the para-toluene sulphonic acid ester of diazotised 1:8-amino - naphthol - 3:6-disulphonic acid and 1-amino - 2 - methoxy-5-methylbenzene (saponified)	monomethylaniline	red		F
23	„	dimethylamine	„		F
24	„	1:4-diamino-benzene	„	F, developed with nitrite and $\beta$ -naphthol	

TABLE I. (cont.)

No.	Compound A	Compound B	Dyeing on cellulose fibres	After-treatments:	
				Me = Metal salts	F = Formaldehyde, etc.
25	Dyestuff from the para-toluene sulphonic acid ester of diazotised 1:8-amino - naphthol - 3:6-disulphonic acid and 1-amino - 2 - methoxy-5-methylbenzene (saponified)	5-amino-2-(2 <sup>1</sup> -oxy-3 <sup>1</sup> - carboxy - 5 <sup>1</sup> -sulphophenyl)-1:3-benztriazole (which can be prepared by the method given in, e.g., Berichte 54, 2195)	red	Me	
26	"	5-amino-2-(4 <sup>1</sup> -oxy-3 <sup>1</sup> - carboxy - 5 <sup>1</sup> -sulphophenyl)-1:3-benztriazole (which can be prepared by the method given in, e.g., Berichte, 54, 2195)	"	Me	F
27	4 - amino-2 <sup>1</sup> -oxy-2-methoxy - 1:1 <sup>1</sup> -azobenzene-5 <sup>1</sup> -sulphonic acid	aniline	brownish yellow	Me	
28	anthranilic acid → 2-(3 <sup>1</sup> -aminobenzoyl) - amino-5 - oxynaphthalene - 7-sulphonic acid	aniline	reddish orange	Me	
29	Dyestuff from the para-toluene sulphonic acid ester of diazotised 1:8-aminonaphthol - 3:6-disulphonic acid and 1-amino - 2 - methoxy - 5-methylbenzene → 2 - amino-5-oxynaphthalene-7-sulphonic acid (saponified)	"	blue	Me	

TABLE II.

Dyestuffs of the general formula:



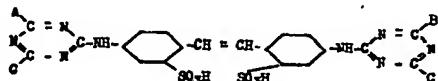
No.	Compound A	Compound B	Dyeing on cellulose fibres	After-treatments:	
				Me = Metal salts F = Formaldehyde, etc.	
1	4-amino-4 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azo- benzene - 3 <sup>1</sup> - carboxylic acid	aniline	yellow	F	Me
2	4-amino-5-methoxy-1:1 <sup>1</sup> - azobenzene-3 <sup>1</sup> -carboxylic acid	dimethylamine	greenish yellow	F	
3	„	aniline	„	F	
4	„	3-amino-acetanilide	„	F, saponified and developed with 1- phenyl - 3 - methyl- 5-pyrazolone	
5	2-naphthyl - amine-4:8- disulphonic acid → 3- diaminobenzene aminoacetanilide	1 - chloro - 2:4- diaminobenzene	reddish yellow	F, developed with 1 - phenyl - 3 - methyl - 5-pyrazo- lone	
6	4-amino-4 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azo- benzene - 3 <sup>1</sup> - carboxylic acid	3-amino-acetanilide	greenish yellow	F, saponified and developed with 1- phenyl - 3 - methyl- 5-pyrazolone	
7	4-amino-4 <sup>1</sup> -acetylamino- 5 - methoxy - 2 - methyl- 1:1 <sup>1</sup> - azobenzene - 3 <sup>1</sup> - sulphonic acid	aniline	yellow	F, saponified and developed with 1- phenyl - 3 - methyl- 5-pyrazolone	
8	4 - amino-2-acetylamino- 4 <sup>1</sup> - chloro-1:1 <sup>1</sup> -azoben- zene-3 <sup>1</sup> -sulphonic acid	„	„	F	
9	„	4 <sup>1</sup> - amino - 5:6 <sup>1</sup> - dimethyl - 4 - oxy- diphenyl - methane 3-carboxylic acid (which can be pre- pared by condens- ing chloromethyl- o - cresotinic acid with m-toluidine by the method described in Speci- fication No. 265,203)	„	F	Me

TABLE II. (cont.)

No.	Compound A	Compound B	Dyeing on cellulose fibres	After-treatments:	
				Me = metal salts	F = Formaldehyde, etc.
10	4 - amino - 2 <sup>1</sup> - oxy - 2- methoxy - 1:1 <sup>1</sup> - azoben- zene-5 <sup>1</sup> -sulphonic acid	aniline	brownish yellow		F Me
11	Dyestuff from the para- toluene sulphonic acid ester of diazotised 1- amino-8-oxynaphthalene- 3:6 - disulphonic acid and 1-amino-2-methoxy- 5-methylbenzene (saponi- fied)	3-amino-acetanilide	red	F, developed with nitrite and $\beta$ - naphthol	
12	1 - (3 <sup>1</sup> - aminobenzoyl)- amino - 4 - oxy - 3 - carb- oxy-benzene-5-sulphonic acid $\rightarrow$ 1 - amino - 3- methyl - 6 - methoxyben- zene.	aniline	reddish yellow		Me
13	"	1-amino - 4 - oxy- benzene - 3 - carb- oxylic acid	reddish yellow		Me
14	1 - (4 <sup>1</sup> - aminobenzoyl)- amino - 4 - oxybenzene- 3-carboxylic acid $\rightarrow$ 1- amino - 3 - methyl - 6- methoxybenzene	aniline	"		Me

TABLE III.

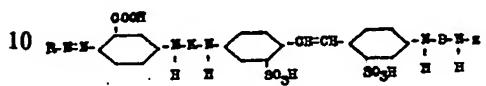
Dyestuffs of the general formula



No.	Compound A	Compound B	Compound C	Dyeing on cellulose fibres	After treatments:	
					Me = metal salts	F = formaldehyde, etc.
1	4 - amino-2-acetylamino-4 <sup>1</sup> - chloro - 1:1 <sup>1</sup> - azo- benzene - 3 <sup>1</sup> - sulphonic carboxylic acid	1 - amino - 4- oxybenzene-3- benzene - 3 <sup>1</sup> - carboxylic acid	aniline	yellow	F	Me
2	Dyestuff from the para-toluene sulphonic acid ester of 1:8 - amino-naphthol-3:6-disulphonic acid and 1 - amino - 2-methoxy - 5 - methylbenzene (saponified)	4 - amino - 3-methoxy-1:1 <sup>1</sup> -ester of 1:8 - amino-azobenzene-3 <sup>1</sup> -naphthol-3:6-disulphonic carboxylic acid	,,	yellowish red	F	
3	,,	4 - amino-4 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azobenzene - 3 <sup>1</sup> -carboxylic acid	,,	,,	Me	F
4	,,	,,	1 - amino - 4- oxy - benzene-3 - carboxylic acid	,,	Me	F
5	4-amino-4 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azobenzene - 3 <sup>1</sup> - carboxylic acid	4 - amino - 2-methoxy - 2 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azobenzene - 5 <sup>1</sup> -sulphonic acid	aniline	brownish yellow	Me	
6	,,	4 - amino-2:5-dimethoxy-2 <sup>1</sup> -oxy-1:1 <sup>1</sup> -azobenzene - 5 <sup>1</sup> -sulphonic acid	,,	brown-yellow	Me	

Similar dyestuffs can be obtained by replacing the 4:4<sup>1</sup>-diaminostilbene-2:2<sup>1</sup>-disulphonic acids mentioned in the foregoing Tables by other stilbene or dibenzyl derivatives.

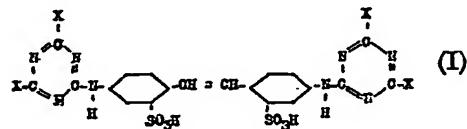
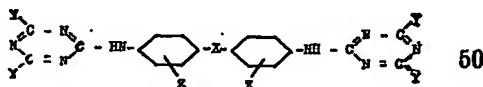
Specification No. 578,014 claims a manufacture of azo-dyestuffs of the general formula



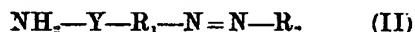
in which R stands for the residue of a compound having a keto-group capable of enolisation. K and B may be, *inter alia*, the residue of a cyanuric halide and N—Z

—H— stands for the residue of a yellow 15 aminoazo-dyestuff which contains at least once an atomic grouping imparting thereto the capacity for forming complex metal compounds, by a method known to be suitable for making azo-dyestuffs of 20 that type.

Specification No. 595,181 claims a manufacture of azo-dyestuffs of the general formula



5 in which three of the X's represent residues of aminoazo-dyestuffs of the general formula



in which R<sub>1</sub> and R<sub>2</sub> represent aromatic 10 nuclei of the benzene series, the NH<sub>2</sub>-Y- group and the -N=N- linkage being in para-position relatively to one another, and R<sub>2</sub> containing a hydroxyl group in ortho-position to a 15 carboxyl group, and

Y represents a direct linkage between NH<sub>2</sub> and R<sub>1</sub> or an atomic grouping of the formula



20 in which one Z represents the linkage connecting this atomic grouping to the NH<sub>2</sub> group, and the other Z represents a hydrogen atom, and in which the NH<sub>2</sub> group is attached to R<sub>1</sub>, and in which the 25 other X represents the residue of any desired aminoazo-dyestuff, wherein 2 mols. of a 1:3:5-trihalogen-triazine are condensed with 1 mol. of 4:4'-diamino-stilbene-2:2'-disulphonic acid, and the 30 product so obtained is condensed with 3 mols. of the same or different amino-azo-dyestuffs of the said general formula (II) and with 1 mol. of any desired aminoazo-dyestuff.

35 It is to be understood that no claim is made herein for the manufacture of azo-dyestuffs of the aforesaid general formulæ of Specifications Nos. 578,014 and 595,181.

40 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that, subject to the foregoing disclaimer, what we claim 45 is:

1. A manufacture of new dyestuffs or intermediates of the stilbene or dibenzyl series by treating a condensation product of the general formula

in which X represents -CH=CH- or -CH<sub>2</sub>-CH<sub>2</sub>-

Y represents a halogen atom, and both of the Z's represent H or -COOH or -SO<sub>3</sub>H, with at least one aromatic 55 amine so as to exchange at least one halogen atom for the residue of an amino-azo-compound or for the residue of an amine which, after the exchange, is capable of forming azo-dyestuffs, and 60 exchanging any other halogen atoms for amino groups and/or for the residues of amines, which may be identical or different and may contain azo-groups, by treatment with ammonia and/or amines. 65

2. A manufacture as claimed in claim 1, wherein the Z's in the general formula represent -SO<sub>3</sub>H and are in the 2:2'-position.

3. A manufacture as claimed in claim 70 1 or 2 wherein the components are so chosen that at least one component, if desired after reaction to form an azo-compound, contains a group which enables metallisation to be brought about 75 on the fibre or in substance.

4. A manufacture as claimed in claim 1 or 2 wherein at least one of the aromatic amines used contains a group suitable for the formation of azo-dyestuffs or a substituent convertible into such a group, and the resulting condensation product, when necessary after modification of a convertible substituent, is converted into an azo-compound by coupling with any 85 desired diazo-component or by diazotising and coupling with any desired azo component, the formation of such external dyestuff being conducted, if desired, on the fibre. 90

5. A manufacture of new dyestuffs or intermediates of the stilbene or dibenzyl series conducted substantially as described in any one of Examples 1-21 herein or with reference to the Tables herein. 95

6. New dyestuffs or intermediates of the stilbene or dibenzyl series whenever prepared or produced by the process of manufacture particularly described and ascertained herein or by any process which 100 is an obvious chemical equivalent thereof.

Dated this 31st day of August, 1944.

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